Tailoring Electrochromic Properties using Poly(*N*-vinylcarbazole) and Poly(*N*-phenyl-2-(2′-thienyl)-5-(5″-vinyl-2″-thienyl)pyrrole) Blends

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Received August 11, 1997; Revised Manuscript Received February 24, 1998

ABSTRACT: Blends of poly(*N*-phenyl-2-(2′-thienyl)-5-(5″-vinyl-2″-thienyl)pyrrole) (**PSNPhS**) and poly(*N*-vinylcarbazole) (**PVK**) were prepared in mass ratios of 1:4, 3:2, and 4:1. Their electrochromic properties were characterized using cyclic voltammetry, in situ spectroelectrochemistry, and spectrocolorimetry. Solid-state electrochromic devices were prepared using ITO/Mylar substrates and a solid polymer electrolyte, with cast films of the polymer blends deposited on the working electrode. The color contrasts of these devices were measured by spectrocolorimetry conforming to the Commission International de l'Eclairage (CIE) methods. The observed color changes in the p-doped state of the devices were compared using the CIE color coordinate values and correlate ($R^2 = 0.97$) with the quantity of **PSNPhS** present in the blend. These combinations of **PSNPhS** and **PVK** yielded colors similar to those of natural vegetation and soils, as desired.

Introduction

The ability to tune the color constitutes one of the important goals in the design of electrochromic devices. Organic materials are attractive for such purposes since a wide range of colors can result from variations in molecular structure.[1] Among these materials, conjugated polymers, especially those based on polythiophenes, have been investigated in much detail.[2] Recently the class of electrochromic materials based on nonconjugated polymers containing pendant π groups have been identified as offering some advantages over the conjugated polymers due to the distinct color contrasts that result from definitive structures of the radical cations that are formed upon doping.[3] A further advantage of these systems lies in their processibility. Although there have been reports of multicolor electrochromic materials, it is unusual for one conducting polymer to exhibit an electrochromic change covering the entire visible region.[4,5] A simple method of achieving a wide range color change might result from a combination of two electrochromic conducting polymers or an electrochromic polymer with another electrochromic material, each covering a different color change region.[6] Earlier reports on such combinations have employed both electrochemical and, to a lesser degree, chemical methods of synthesis.[6,7]

Previous work in our laboratory has shown that copolymers can be used to modify the color of electrochromic devices, and we were able to correlate the observed color change with the stoichiometry of the comonomers in these systems.[8] We wished to determine if such color changes could also be obtained by making *blends* of two polymers exhibiting different electrochromic properties since this method might lead to more facile modifications of the color. To test this we chose poly(*N*-vinylcarbazole), **PVK**, an electrochromic material that is green in the doped state and colorless in the neutral state,[9,10] and another polymer we recently reported on, poly(*N*-phenyl-2-(2′-thienyl)-5-(5″-vinyl-2″-thienyl)pyrrole), **PSNPhS**, whose color changes from yellow to reddish brown when oxidized.[8] Both these systems are nonconjugated polymers containing pendant π groups. In this paper we discuss the electrochromic properties of three polymer blends with different ratios of **PVK** to **PSNPhS** and their potential for generating the colors of vegetation and soils observed in nature.

Experimental Section

All reagents were ACS reagent grade and used without further purification. All compounds were characterized by UV, IR, ^{1}H NMR spectroscopy and elemental analysis. Poly(*N*-vinylcarbazole) ($M_w = 1\,100\,000$) was purchased from Aldrich Chemicals Inc. The general synthetic routes for the monomers and polymers are outlined in Scheme 1.

Synthesis of *N*-Phenyl-2,5-bis(2-thienyl)pyrrole (Ib). To 10 mmol of 1,4-bis(2-thienyl)-1,4-butanedione (**Ia**) in 50 mL of benzene were added 11 mmol of freshly distilled aniline and a catalytic amount of *p*-toluenesulfonic acid. This mixture was refluxed overnight, and the water formed in the reaction was separated using a Dean−Stark condenser. The reaction mixture was cooled, washed with saturated $NaHCO_3$ solution, and dried over magnesium sulfate, and the solvent was removed at reduced pressure. The solid thus obtained was chromatographed on silica gel (60−230 mesh) using a hexane−ethyl acetate (20:1) solvent system followed by recrystallization from methanol. The yield of the pure compound **Ib** was 30%. Mp: 173−174 °C.

^{1} H NMR ($CDCl_3$), δ: 7.37 (m, 5H, phenyl), 7.03 (d, $J = 4.9$ Hz, 2H, pyrrole), 6.79 (t, $J = 3.66$ Hz, 2H, thienyl), 6.5 (t, $J = 4.9$ Hz, 4H, thienyl).

Synthesis of *N*-Phenyl-2-(2′-thienyl)-5-(5″-formyl-2″-thienyl)pyrrole (Ic). Phosphorus oxychloride (20 mmol) was added to 20 mL of dimethyl formamide (DMF) at 0 °C and the mixture was stirred for 15 min. A solution of **Ib** (20 mmol) in 15 mL of DMF was then added to this solution over a period of 30 min. at 0° C. The mixture was stirred overnight and heated at 70° C for 1 h after which the reaction mixture was cooled and poured into ice. The precipitated product was filtered, dried over magnesium sulfate, and column chromatographed over silica gel using a 1:6 ethyl acetate−hexane solvent system. The yield of the aldehyde was 70%. Mp 208−210 °C.

^{1}H NMR($CDCl_3$) δ: 9.78 (s, 1H, aldehyde), 7.32 (m, 5H, phenyl), 7.24−6.89 (m, 7H, thienyl and pyrrole).

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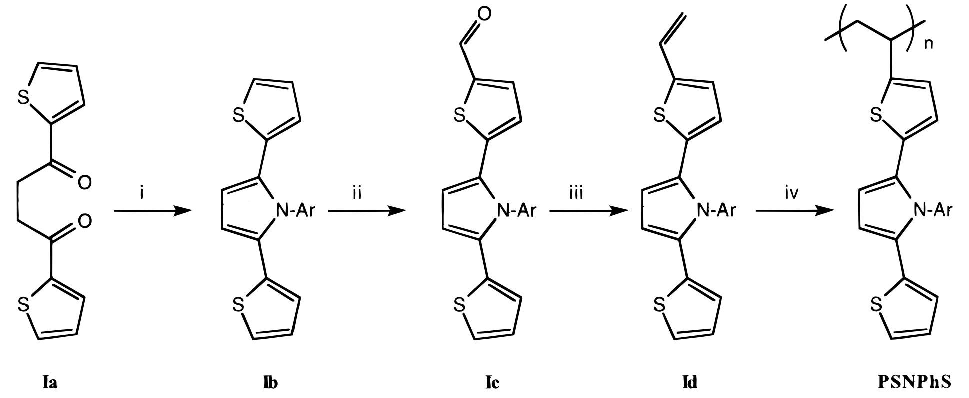
S0024-9297(97)01212-6 CCC: $15.00

Scheme 1. Synthesis of Poly(*N*-phenyl-2-(2′-thienyl)-5-(5″-vinyl-2″-thienyl)pyrrole)



Ar = C_6H_5

i: Aniline, *p*-toluenesulfonic acid (cat); ii: $POCl_3$, DMF; iii: CH_3PPh_3Br, *n*-BuLi; iv: BF_3-etherate, CH_2Cl_2

Synthesis of *N*-Phenyl-2-(2-thienyl)-5-(5″-vinyl-2″-thienyl)pyrrole (Id). *n*-Butyllithium (5 mmol) was added slowly to a solution of 5 mmol of methyltriphenylphosphonium bromide in dry THF (25 mL) under N_2, and the mixture was stirred for 3 h. A solution of 5 mmol of **Ic** in THF (80 mL) was then added dropwise, and the resulting mixture was stirred for 24 h. The reaction mixture was poured into ice water, and the product was extracted into ethyl ether several times. The organic layer was washed with water, dried over magnesium sulfate, and evaporated. The resulting solid was purified by chromatography on silica gel using a 1:6 ethyl acetate–hexane solvent system. The compound was recrystallized from methanol to give pale yellow crystals (mp 135–136 °C) in 60% yield.

^{1} H NMR(CDCl$_3$), δ: 7.39–7.15 (m, 5H, phenyl), 7.11 (d, 3.9 Hz, 2H, pyrrole), 6.93–6.49 (m, 5H, thienyl), 5.59 (dd, 17.2 Hz, 1H, vinyl α), 5.09 (dd, 10 Hz, 2H, vinyl β).

Anal. Calcd for $C_{20}H_{15}NS_2$: C, 72.04; H, 4.53; N, 4.20; S, 19.23. Found: C, 72.22; H, 4.60; N, 4.12; S, 19.06.

Synthesis of Poly (*N*-phenyl-2-(5′-vinyl-2′-thienyl)-5-(2″-thienyl)pyrrole) (PSNPhS). The cationic polymerization was carried out in a degassed dichloromethane solution containing monomer (**Id**, 50 mmol), and BF_3–etherate (0.9 mmol) at 0 °C for 8 h. The polymer was purified by reprecipitation from THF/*n*-hexane. $M_w = 3412$; $M_n = 2867$.

^{1}H NMR(CDCl$_3$), δ: 7.3–6.42(broad, aromatic), 1.7–1.4 (broad, alkyl)

Preparation of Electrochromic Devices. Polymer blends were prepared by mixing various mass ratios of **PVK** and **PSNPhS** in chloroform. The compositions of various blends are as follows: blend **I**, **PSNPhS:PVK** (1:4); blend **II**, **PSNPhS:PVK** (3:2); blend **III**, **PSNPhS:PVK** (4:1).

These solutions (2 mL at 4% w/v in chloroform) were cast onto 15 cm × 6 cm ITO/Mylar strips (Altair O, Southwall Technologies, Inc.) using an Acculab Jr. 30 casting rod, and the polymer films were air-dried before assembling them into the device. The electrochromic material cast onto ITO serves as working electrode in the electrochromic device and a blank Altair O strip serves as counter electrode. The polymer electrolyte was prepared by mixing poly(methyl methacrylate) (M_w 120 000) (500 mg), propylene carbonate (1 mL), ethylene carbonate (2 g), and lithium tetrafluoroborate (100 mg) in acetonitrile (3 mL). The electrolyte was spun cast onto the blank ITO and the device was assembled in a sandwich manner (Figure 1).

Reflectance and Color Measurements. The reflectance spectra and color measurements were performed on a HunterLab MiniScan XE spectrocolorimeter with the large view area option to record diffuse reflectance using a D65 Daylight illuminant. The MiniScan system is controlled through a computer interface using HunterLab Universal software. The color data is displayed in CIE 1976 *L*a*b** coordinates using the CIE 1964 10 degree standard observer model. In this opponent color scale coordinate system *L** indicates the intensity of the reflected light and the *a** coordinate indicates a change from red (positive direction) to green (negative direction) while the *b** coordinate indicates a color change from yellow (positive direction) to blue (negative direction) (Figure 2). The MiniScan XE records the spectral reflectance over the range 400–700 nm, with a resolution of 10 nm and a wavelength accuracy of 1 nm. The CIE coordinates are then extracted from the components of the reflected light.

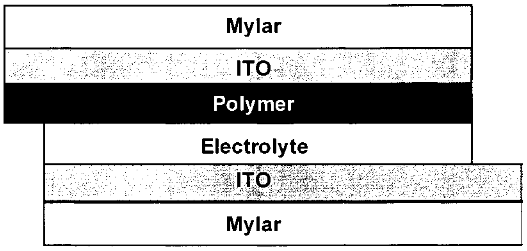


Figure 1. Typical assembly of an electrochromic device.

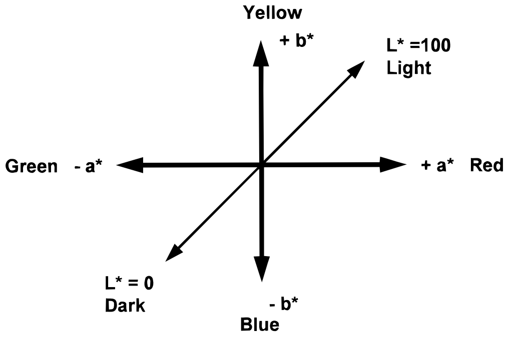


Figure 2. The CIE *L* a* b** opponent color scale.

Variability in thickness of polymer films between devices causes some variation in the CIE *L*a*b** coordinates. Three devices of each blend were constructed and a series of doping/dedoping experiments were performed. Typically 10 measurements were acquired and averaged for the doped and neutral state of each device producing a standard deviation ±1 % for each color coordinate measurement.

Electrochemical and Spectroelectrochemical Studies. Cyclic voltammetry was conducted using a EG&G PAR 263 potentiostat. The voltammograms were collected using the Research Electrochemistry Software (version 4.0, EG&G Instruments Inc.) on a IBM-compatible 486 personal computer. The polymers were deposited onto the electrode (Altair O) by casting from chloroform solutions. The cyclic voltammograms

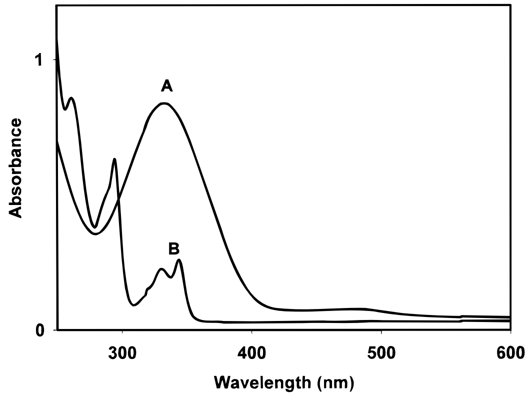


Figure 3. Absorption spectra of the homopolymers in their neutral state in a chloroform solution. A: **PSNPhS**; B: **PVK**.

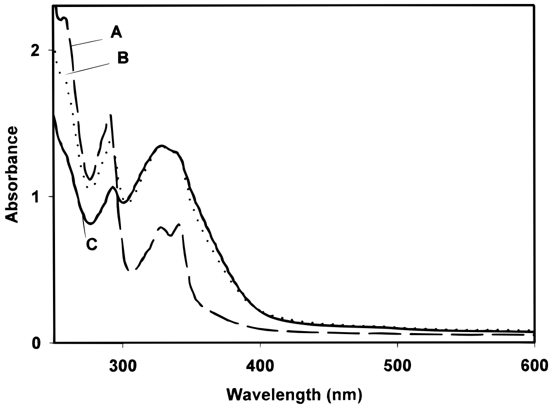


Figure 4. Absorption spectra of chloroform solutions of blends in their neutral state. A, blend **I**; B, blend **II**; C, blend **III**.

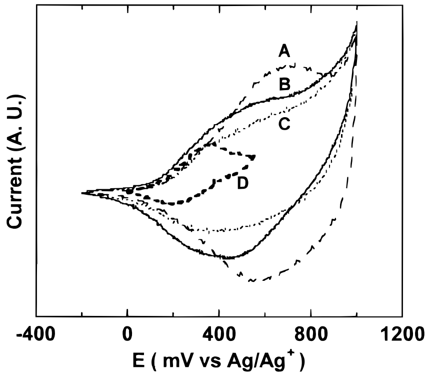


Figure 5. Cyclic voltammograms of **PSNPhS**:**PVK** blends deposited on Pt electrodes cycled between −300 and +1000 mV vs Ag/Ag$^+$ at a scan rate of 50 mV s^{-1}: A, blend **I**; B, blend **II**; C, blend **III**; D, blend **III** cycled to 500 mV.

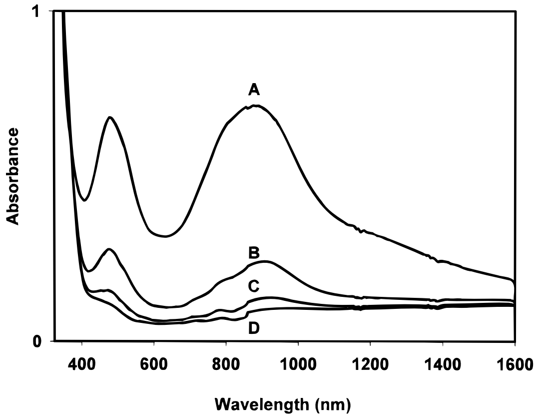


Figure 6. In situ spectroelectrochemistry of blend **I** at the following potentials vs Ag/Ag$^+$: A, 1.0 V; B, 0.9 V; C, 0.8 V; D, 0.0 V.

are not compensated for the IR drop occurring across the face of the ITO electrode. Spectroelectrochemical measurements of the blends were recorded in 0.2 M tetramethylammonium trifluoromethanesulfonate (TMATFMS) in acetonitrile in a specially modified quartz cuvette described previously [9] which incorporated a silver wire pseudo-reference electrode. A cuvette containing a blank Altair O strip in the electrolyte solution was placed in the reference beam of the spectrophotometer. Spectra were recorded on a Perkin-Elmer Lambda 9 between 325 and 1600 nm as a function of incremental changes to the applied potential.

Results and Discussion

Initial ring closure in the synthesis of the **PSNPhS** proceeded in typical yields of about 30%, whereas subsequent Vilsmeyer formylation and Wittig reactions were effected in 60−80% yields. The cationic polymerization was carried out using boron trifluoride with yields up to 55%. (Scheme 1). The absence of vinylic protons in the region of δ 5−5.6 ppm in the proton nmr supports the polymerization via vinylic groups. This is further supported by the FT- IR spectra of the polymer which showed the absence of peaks at 1620 and 980 cm^{-1} corresponding to the monomer's olefinic C−H stretch and bending vibrations, respectively. The low molecular weight observed in this polymer is in agreement with the literature values for similar systems.[3b]

The absorption spectra of the constituent homopolymers are shown in Figure 3. The spectrum of the **PVK** homopolymer between 250 and 700 nm consists of 3 peaks at 290, 328, and 340 nm. The **PSNPhS** homopolymer has a broad absorption in the same region with a peak maximum at 334 nm. The ratio of the areas under the peaks at 290 and 340 nm in the absorbance spectra of the neutral polymer blends (Figure 4) relate well with the ratios of the individual homopolymer components. The polymer blends exhibit little absorbance in the visible spectrum in the neutral state.

Cyclic voltammograms of the polymer blends are shown in Figure 5. Curve D, obtained when the potential is cycled to only 500 mV vs Ag/Ag$^+$ for **PSNPhS**-rich blend III, displays the reversible redox couple of **SNPhS**. Upon multiple scanning to 1.0 V, a second wave due to the oxidation of the carbazole functionality appears around 0.7 V and stabilizes in intensity after a few cycles. This wave is most evident for blend I, which is **PVK**-rich.

In situ spectroelectrochemistry was performed on all the blends. The spectral changes observed with an incremental increase in the potential for blend **I** are shown in Figure 6 and are typical. Two new peaks occur upon doping, one in the visible region at 480 nm and the second peak in the NIR region at 875 nm. The peak at 480 nm is ascribed to the absorption by radical cations of both species whereas the peak at 875 nm may be due to the radical cations of six ring species formed upon cross-linking in the case of **PSNPhS** and/or the carbazole diad in the case of **PVK**.[8,9,11] The broad nature of the absorption peaks suggests the overlap of the characteristic absorptions of both **PVK** and **PSNPhS**.

Color Trends and Difference Spectra. CIE 1976 $L^*a^*b^*$ coordinates for homopolymers and blends in the doped and neutral states are given in Table 1. To the observer the neutral state of **PVK** is colorless while **PSNPhS** is yellow. The color of the neutral or dedoped

Table 1. CIE 1976 *L* a* b Coordinates for Homopolymers and Polymer Blends in a Doped State and a Neutral State**

	neutral			doped		
polymer	*L**	*a**	*b**	*L**	*a**	*b**
PVK	82.97	−2.31	16.55	73.74	−5.78	24.16
blend **I**	84.32	−1.35	17.43	76.55	2.99	20.33
blend **II**	78.53	3.16	25.52	69.63	7.01	24.22
blend **III**	75.51	5.68	26.65	55.42	10.16	26.13
PSNPhS	78.79	4.73	27.47	57.69	16.12	33.33

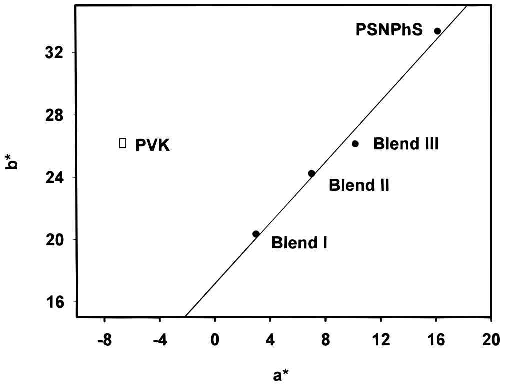


Figure 7. Correlation ($R^2 = 0.97$) between *a** and *b** parameters of polymer blends and homopolymers in the limiting (maximum reversible) doped states.

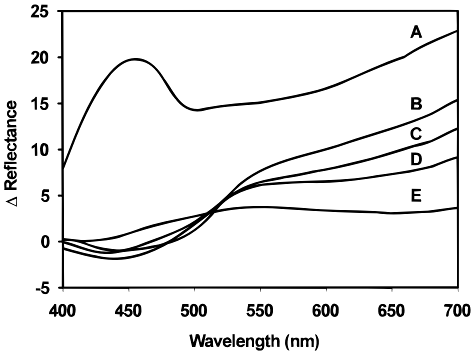


Figure 8. Differences in reflectance spectra for homopolymers and blends referenced to their corresponding doped states: A, **PVK**; B, **PSNPhS**; C, blend **III**; D, blend **II**; E, blend **I**.

polymer blend is dependent on the amount of **PSNPhS** present. The incremental change of the *a** and *b** coordinates for the doped polymer blends can be correlated ($R^2 = 0.97$) with **PSNPhS** composition (Figure 7). The increase of *a** and *b** in the doped state qualitatively indicates a color change toward orange (yellow and red mixture) on the *L***a***b** scale.

Reflectance spectra of the polymer blends provide another method to characterize these systems. In the neutral state these blends show little differences in the reflectance spectra in the visible region, but exhibit distinct differences in the doped states (Figure 8) for which the greatest changes are the appearance of a peak in the green near 550 nm and a broad peak in the red region from 600 to 700 nm. These spectral shifts are in agreement with the in situ spectroelectrochemistry experiments.

The change in reflectance in the green region arises from the doped state of carbazole and the formation of **PSNPhS**-derived moieties influences the red colors. The combination of these two species create the subtle shades of green, brown, and tan colors observed in the devices.

Conclusions

Blends were made using different mass ratios of two nonconjugated polymers containing pendant π groups, namely, poly(*N*-vinylcarbazole) and poly(*N*-phenyl-2-(2′-thienyl)-5-(5″-vinyl-2″-thienyl)pyrrole). The electrochromic properties of these polymer blends were studied and their reflectance spectra were analyzed in terms of CIE *L***a***b** coordinates. The electrochromic properties of these blends can be controlled by modifying the ratio of the individual components of the blends, and provides a simple and effective technique for tailoring the color. Furthermore these blends successfully generate the desired range of brown, tan, and green colors often found in natural vegetation and soils. We are extending this approach by blending **PVK** and **PSNPhS** with additional electrochromic materials in order to create a wider variety of colors.

Acknowledgment. This work was supported by U. S. Army Engineer Waterways Experiment Station.

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MA971212S